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## Second-Harmonic Generation from Floating Monolayers and Langmuir–Blodgett Multilayers of Poly(isocyanide)s

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**ABSTRACT:** Floating monolayers as well as Langmuir–Blodgett (LB) films of poly(isocyanide)s containing NLO-active side chains appear to be capable of generating second-harmonic light. Spin-coated films and cast films of these polymers do not show this behavior. These results indicate that the NLO activity of the LB films originates from the orientation of the side chains obtained at the air–water interface. In the case of poly(isocyanide)s with relatively hydrophobic side chains the second-harmonic intensities generated from the LB films are small, probably because the films are of the Y-type. Poly(isocyanide)s with more hydrophilic side chains form LB films which are Z-type. These films show stable second-harmonic generation without the need of poling with high electrical fields at high temperatures.

### Introduction

One of the major challenges in the development of organic materials for applications in second-order nonlinear optics is to induce and retain the required non-centrosymmetric macroscopic structure.<sup>1</sup> Although electric field poling of films, particularly of polymers containing nonlinear optical chromophores, has been shown to be a successful method, the degree of molecular orientation achieved is still rather low and it requires careful tailoring to maintain the induced alignment in the absence of the field.<sup>2,3</sup> It is attractive to build up the desired oriented films by molecular engineering techniques in such a way that the active chromophores can directly and spontaneously adopt the desired non-centrosymmetric geometry. For this reason many research groups have recently applied the Langmuir–Blodgett (LB) assembly technique, in which hydrophilic and hydrophobic interactions of amphiphilic molecules at the air–water interface induce orientational order, to fabricate such films.<sup>4</sup> This by itself is a complex task. It requires the incorporation of different functionalities in the same molecule and the need to consider properties of different materials, such as temporal and thermal stability, optical quality, and compatibility. It also requires insight in how to achieve the desired orientational order. Multilayer films prepared by LB assembly can have two general kinds of molecular structure in adjacent layers. One is a polar orientation in which the hydrophilic portions of the molecules in one layer are oriented adjacently to the hydrophobic regions of the molecules in the next layer.<sup>5</sup> This is the desirable structure for second-order nonlinear optics, since the film is inherently non-centrosymmetric. In the other kind of molecular structure the hydrophobic parts of two adjacent layers are facing each other, resulting in a LB film structure which is centrosymmetric.

In this study we use poly(isocyanide)s with large NLO-active side chains containing either a hydrophobic or a hydrophilic moiety in the outer core of the polymer structure to prepare LB films. The NLO-active chromophores in the side chains are able to bend toward the water surface. In the case of the hydrophilic side chains this results in sufficient interaction with the subphase to ensure a polar orientation. As we will show, thick films can be prepared of which the nonlinear optical activity does not diminish because of orientation losses.

### Experimental Section

**Materials.** The route which was used to synthesize the different polymers is given in Scheme 1. Together with Table 1, Scheme 1 shows which precursors and polymers were synthesized and investigated in this study.

**Synthesis.** The general procedures have been outlined elsewhere.<sup>6</sup> A detailed description of the procedures is available on request in the supporting information.

**NLO Measurements.** The NLO activity of floating Langmuir layers was determined by measuring the generated second-harmonic intensity using the setup described by S'heeren et al.<sup>8</sup> and using silver as a reference.<sup>9</sup>

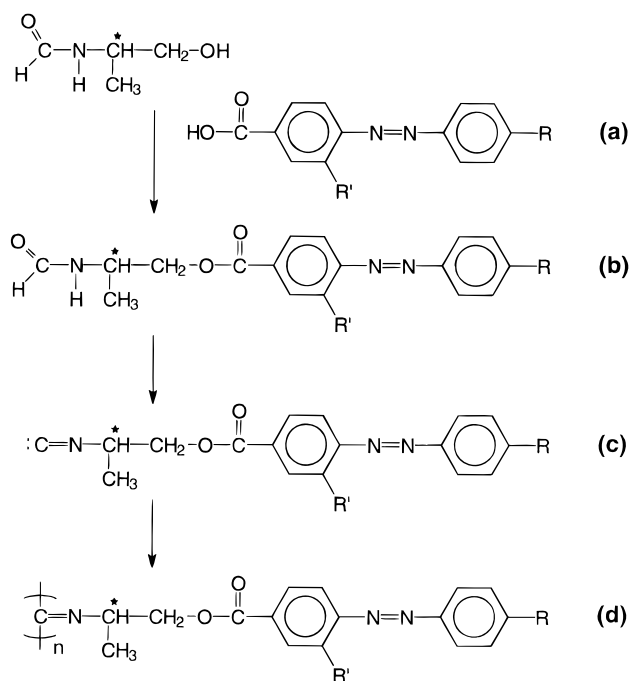
The NLO activity of LB films was determined by measuring the second-harmonic intensity generated from multilayered samples on glass substrates, using the setup described by Cnossen et al.<sup>10</sup> The second-harmonic intensity was referenced to a clean silver mirror (100% reflectance) with  $\chi^{(2)} = 1.3 \times 10^{-9}$  esu (at  $p_{\text{incidence}} - p_{\text{detection}}$  polarization setting).<sup>9</sup> For conversion into SI units one can use, in the case of  $\beta$ , the relationship  $1 \text{ Cm}^3\text{V}^{-2} = 2.7 \times 10^{20}$  esu and, in the case of  $\chi^{(2)}$ ,  $1 \text{ CV}^{-2} = 2.7 \times 10^{14}$  esu.

### Results and Discussion

In our experiments the square root of the second-harmonic intensity was plotted as a function of the number of layers  $n$ . In the case of optically transparent films with thicknesses less than  $\lambda$  (532 nm), one expects a linear relationship between the two variables as shown in eq 1. However, in the case of films which

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Scheme 1

Table 1. Polymers and Their Precursors Used in This Study<sup>a</sup>

compd	R	R'	config at C*
<b>8a-d</b>	N( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>	H	<i>R,S</i>
<b>9a-d</b>	N( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>	H	<i>S</i>
<b>10a-d</b>	N( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub>	NO <sub>2</sub>	<i>S</i>
<b>11a-d</b>	N(C <sub>2</sub> H <sub>4</sub> OC(O)CH <sub>3</sub> ) <sub>2</sub>	NO <sub>2</sub>	<i>S</i>
<b>12a-d</b>	morpholino	NO <sub>2</sub>	<i>R,S</i>

<sup>a</sup> For structures see Scheme 1.

display absorption at the doubled frequency, *i.e.*, at  $\lambda = 532$  nm, the second-harmonic intensity  $I_{2\omega}$  generated from the film is diminished because of absorption occurring in the film itself. The expression for the generated second-harmonic light in that case has to be changed, *i.e.*, in such a way that it includes the absorption factor  $I = I_0 \times 10^{-\epsilon dn}$ , where  $\epsilon$ ,  $d$ , and  $n$  denote the extinction coefficient, thickness of one layer, and number of layers, respectively (eq 2).

$$\sqrt{I_{2\omega}} = Cn \quad (1)$$

$$\sqrt{I_{2\omega}} = (Cn) \times 10^{-\epsilon dn/2} \quad (2)$$

The obtained curves were fitted to the function given by eq 2, and the fitting parameter,  $C$ , was used to calculate the different values of the  $\chi^{(2)}$  tensor, *viz.*,  $\chi_{xxx}$ ,  $\chi_{xxz}$ , and  $\chi_{zzz}$ .

**NLO Properties of Poly(isocyanide)s with Hydrophobic Side Chains. Floating Monolayers.** Second-harmonic generation (SHG) measurements were carried out approximately 15 min after the desired surface pressure had been reached and the film area had become constant. Second-order susceptibilities were calculated from the experimental data using the procedure of Dick et al.,<sup>11</sup> neglecting the refractive index of the floating monolayer, *i.e.*,  $n_{\text{film}} = n_{\text{water}} = 1.32$ .

The results of the measurements of the second-harmonic generation on floating monolayers of polymers **8** and **9** and mixed monolayers of **10** and **AB**<sup>12</sup> (amylose butyrate) are compiled in Table 2. For the calculations it was assumed that the monolayer thicknesses of

Table 2. Second-Order Susceptibilities of Monolayers of Polymers **8** and **9** and Mixed Monolayers of **10** and **AB**

polymer	mole fraction of poly(isocyanide)	$\pi$ (mN/m)	$\chi_{xxx}$ (10 <sup>-9</sup> esu)	$\chi_{zzz}$ (10 <sup>-9</sup> esu)
<b>8</b>	1.00	10	5.5	22.0
<b>9</b>	1.00	10	7.4	27.7
	1.00	15	8.1	27.7
<b>10/AB</b>	0.28	15	9.8	34.1
		25	15.7	56.6
	0.66	15	10.0	37.7
		25	12.9	49.4
	1.00	15	9.5	44.6

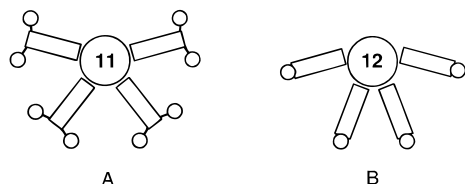
polymers **8** and **9** were the same as those of polymer **10**, *i.e.*, 2.73 nm.<sup>12</sup> The fact that the nitro group which is present in polymer **10** is completely buried within the side chains makes this assumption valid.

The  $\chi_{xxx}$  and  $\chi_{zzz}$  values of polymer **9** measured at  $\pi = 10$  mN/m were slightly higher than those of polymer **8**. One might conclude from this result that a poly(isocyanide) prepared from an optically pure monomer (polymer **9**) gives rise to an enhancement of the second-harmonic signal. One should, however, take into account that the error in the experiments is approximately 25%. In other words: One may not conclude from these measurements that polymer **9** adopts a more non-centrosymmetric structure at the air-water interface than the racemic polymer **8**.

At a surface pressure of 15 mN/m, polymer **9** displayed nearly the same  $\chi^{(2)}$  values as at a surface pressure of 10 mN/m. For a well-behaved monolayer, with all side chains located at the air-water interface, one would expect that the  $\chi^{(2)}$  values become larger at higher surface pressure, simply because in the latter case more chromophores are present per unit area. Probably the monolayer of **9** is pushed into thicker domains in which the chromophores adopt a random orientation. At a low surface pressure these domains are smaller and less numerous than at a higher surface pressure. This explanation would be in agreement with the morphology of the floating film, as revealed by electron microscopy<sup>12</sup> for the comparable polymer **10**.

For the mixed monolayer of polymer **10** and **AB**,  $\chi_{zzz}$  increased with increasing amount of **10** in the film (Table 2). The increase was, however, smaller than expected for polymers that are completely located at the air-water interface. As was shown earlier by us,<sup>12</sup> not all segments of polymer **10** are situated at the interface, which may explain why the increase is relatively small. Changing the surface pressure from 15 mN/m to 25 mN/m gave rise to higher  $\chi^{(2)}$  values. The floating layer composed of 66% polymer **10** showed lower  $\chi^{(2)}$  values than the layer composed of 28% polymer **10**. This result can be explained only if we assume that the former layer contains regions in which the chromophores have a random orientation. Such regions may arise if the floating layer forms thick fluid-like droplets or when it is in a collapsed state.<sup>12</sup>

**LB Multilayers.** The NLO activities of films of polymers **8** and **9** and mixed films of **10** and **AB** were determined by measuring the second-harmonic intensity generated by multilayered samples on glass substrates.<sup>10</sup> Poly(isocyanide)s prepared from racemic mixtures of monomers are not expected to generate any second-harmonic signal. Nevertheless, they displayed a small second-harmonic signal, which may be the result of irregularities during the transfer. The LB films probably were not perfectly Y-type and, as a consequence, did not have a perfect centrosymmetrical struc-



**Figure 1.** Schematic representation of the orientations of the side chains of polymers (A) **11** and (B) **12** in the LB film. One helical turn is shown.

**Table 3. Second-Order Susceptibilities of Floating Monolayers of Polymers 11 and 12**

polymer	$\pi$ (mN/m)	$\chi_{xxz}$ ( $10^{-9}$ esu)	$\chi_{zxx}$ ( $10^{-9}$ esu)	$\chi_{zzz}$ ( $10^{-9}$ esu)
<b>11</b>	1	5.5	1.4	27.0
	5	5.7	1.4	32.2
	15	7.2	0.7	43.7
<b>12</b>	1	10.5	5.2	46.8
	5	17.9	4.8	59.9
	15	14.8	1.9	87.1

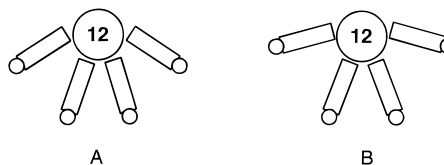
ture. Cast films of the polymers and the polymeric mixtures showed no second-harmonic generation at all, indicating a completely random orientation of the chromophores in this case. Only when the monolayers were transferred onto aluminum or silver substrates was it possible to detect some light with the doubled frequency. In the case of metal surfaces the electrical field at the substrate is increased compared to glass surfaces because electrons present at the metal surface can contribute to the generation of the second-harmonic signal.<sup>13,14</sup> As a correct reference sample for this situation is not available, we were not able to calculate the different components of the  $\chi^{(2)}$  tensor.

**NLO Properties of Poly(isocyanide)s with Hydrophilic Side Chains. Floating Monolayers.** Measurements were performed on polymers **11** and **12** as described in the previous section, and the data are presented in Table 3. Polymer **12** shows higher second-order susceptibilities than polymer **11**, which is understandable because its side chains can have a more parallel orientation than those of the latter polymer. Probably because of the presence of two ester groups per side chain, polymer **11** occupies more space, resulting in a quasi-antiparallel alignment of the chromophores and as a consequence a lower SHG (Figure 1).

It appears that  $\chi_{xxz}$  is higher than  $\chi_{zxx}$  in all cases and that the ratio  $\chi_{xxz}/\chi_{zxx}$  is even larger in the case of polymer **11** compared to polymer **12**. The chromophores in polymer **11** probably have a more parallel orientation with respect to the air–water interface than those in polymer **12**.

Also the distribution of the side chain orientations may be different for the two polymers. Because the chromophores are covalently bound to a rigid polymer backbone, it is useless to calculate their average angle of inclination. They will be restricted in their movements, and some of them will be forced to have orientations that are different from those of other groups.

**LB Multilayers.** The NLO activities of LB multilayers of mixtures of polymers **11** and **12** with **5**<sup>6</sup> were determined on samples deposited on glass substrates. The samples consisted of 6–100 layers of polymer mixtures. The films were found to absorb light at 532 nm, and the second-harmonic intensity was therefore calculated in the same way as described in the previous section. The results are compiled in Table 4.



**Figure 2.** Schematic representation of the orientations of the side chains of polymer **12** in (A) monolayers and (B) LB films.

**Table 4. Second-Order Susceptibilities of Mixed LB Films of Polymers 11 and 12 with Polymer 5**

polymer	mole fraction of dye polymer	$\chi_{xxz}$ ( $10^{-9}$ esu)	$\chi_{zxx}$ ( $10^{-9}$ esu)	$\chi_{zzz}$ ( $10^{-9}$ esu)
<b>11</b>	0.23	3.7	1.3	13.5
	0.44	5.1	2.2	22.3
<b>12</b>	0.15	1.9	0.8	7.5
	0.37	4.6	1.9	18.5
	0.56	7.0	2.9	27.9

Taking into account the different ratios of mixing used in the case of the LB films, the  $\chi^{(2)}$  values are not much different from those determined for the floating monolayers (Table 3). Apparently the non-centrosymmetrical structure, generated at the air–water interface, is maintained in the LB film without loss of orientation. Moreover, the signals appeared to be stable at ambient temperatures for a period exceeding 1 year. Obviously, it is very unfavorable for the film to reorganize toward a centrosymmetric structure because in that case it must increase its thickness, creating a larger fraction of free volume. Solution cast films did not show SHG, indicating that the NLO activity of the LB films originates from a defined orientation of the side chains at the air–water interface.

In the floating monolayers the  $\chi^{(2)}$  values of polymer **12** are approximately 2 times higher than those of polymer **11**. In the case of the LB multilayers the  $\chi^{(2)}$  values match. We explain this from the fact that the orientation of the side chains of polymer **12** in the floating monolayer is slightly more perpendicular to the surface than in the LB film. The extra orientation of the chromophores obtained from the interaction with the water surface is reduced in the LB film where this interaction is lacking. The possible orientations of the side chains of **12** in the different situations are schematically depicted in Figure 2.

## Conclusions

In this study we have shown that rigid-rod polymers substituted with NLO-active chromophores can be successfully applied as building blocks to construct second-order NLO materials with enhanced time and temperature stability of the polar order. In the following we will summarize the most important results of our study.

Contrary to expectation, floating monolayers of the poly(isocyanide)s do not display enhancement of the second-harmonic signal when the polymer is optically active.

LB multilayers prepared from poly(isocyanide)s with relatively hydrophobic side chains exhibit little second-harmonic generation, probably because the orientation of the chromophores in adjacent layers of the multilayered film is antiparallel. The latter is the result of a quasi-Y-type deposition process.

It has been possible to prepare thick LB films from poly(isocyanide)s with NLO-active side chains, which display a preferred orientation of the chromophoric groups. This preferred orientation is obtained at the

air–water interface and is maintained in the multilayered film, leading to stable NLO activity. Our polymers with hydrophilic side chains possess an orientational stability which is unprecedented in nonpoled and non-cross-linked systems.

**Supporting Information Available:** Experimental details of the synthesis of the precursors and polymers used in this study (11 pages). Ordering information is given on any current masthead page.

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